DEVELOPMENT AND CHARACTERIZATION BETWEEN POLYETHERSULFONE/POLYSULFONE (PES/PSF) MICIBLE BLEND WITH PRIMARY POLYMER (PES AND PSF) MEBRANE FOR O_2/N_2 SEPARATION

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ABSTRACT

Membrane technology becomes more interesting in industrial level for gas separation and purification. Main problem in membrane technology industries is hard to find membrane that high performance both in selectivity and permeability. Membrane that provide high permeability offered low selectivity and vice versa. Therefore, blend polymer is introduced to overcome this problem. Means that, beneficial properties of polymers are combining in one single material. In this study, four difference compositions of dope solutions have prepared which are 25% polyethersulfone (PES), 25% polysulfone (PSF), 20% polyethersulfone 5% polysulfone (PES/PSF) and 5% polyethersulfone 20% polysulfone (PES/PSF) in order to prepared the asymmetric membrane. The membrane was fabricated by using dry/wet phase inversion technique. Two type of membrane were produced from each of the sample membrane which are coated and uncoated membrane. The coating membrane was coated by coating agent, polydimethylsiloxane (PDMS). The performance of the membrane was evaluated by gas permeation unit with pure oxygen (O_2) and nitrogen (N_2) as a test gaseous. From the result, PES/PSF blend polymers show the best result compared the others, where the permeability value for O_2 is about 19.93 GPU and N_2 is 14.95 GPU whereas the selectivity of O_2/N_2 is 1.33. The lowest selectivity can be achieved by using primary polymer dope solution of PES and the selectivity for O_2/N_2 is 1.12 where the permeability of O_2 is 91.84 GPU and N_2 is 82.07 GPU. At 25% total polymer show not many difference to the selectivity. This is because only small amount of second polymer was added in order to blend the polymer. Then, the membrane morphology was characterized by Scanning Electron Microscopy (SEM) for identified the surface structure and cross section of the membrane. Cross section for blend polymer show the pore is smallest than primary polymer while surface structure for coated membrane is smooth as compared to uncoated membrane. From this study, by blending two type of polymer increase the performance of the membrane.

ABSTRAK

Teknologi membran menjadi sangat terkenal di peringkat industri dalam proses pemisahan dan penulinan gas. Masalah utama dalam teknologi membran ialah sukar untuk mendapatkan membran yang berprestasi tinggi iaitu membran yang mempunyai kadar pemisahan yang tinggi dan kadar pemilihan yang tinggi dalam masa yang sama. Ini kerana membran yang mmpunyai kadar pemisahan yang tinggi akan mempunyai kadar pemilihan yang rendah dan begitulah sebaliknya. Oleh kerana itu, polimer campuran diperkenalkan bagi menagatasi masalah tersebut. Dalam kaedah ini, kebaikan yang ada pada dua polimer digabungkan menjadi dalam satu bahan. Dalam kajian ini, empat larutan pekat yang berbeza iaitu 25% polyethersulfone (PES), 25% polysulfone (PSF), 20% polyethersulfone 5% polysulfone (PES/PSF) dan 5% polyethersulfone 20% polysulfone (PES/PSF) disediakan untuk menyediakan asymmetric membran. Teknik yang digunakan ialah pembalikan fasa kering/basah. Dua jenis membran dihasilkan daripada semua sampel membran iaitu bersalut dengan agen salutan polydimethylsiloxane (PDMS) dan tidak bersalut. Prestasi semua membran diuji dengan alat penyerapan gas menggunakan gas oksigen (O_2) dan nitrogen (N_2) tulen. Daripada keputusan yang diperolehi, campuran polymer PES/PSF menunjukkan keputusan yang baik daripada yang lain, dimana kadar serapan untuk O_2 ialah 19.93 GPU dan N_2 ialah 14.95 GPU manakala kadar pemilihan O_2/N_2 ialah 1.33. Kadar pemilihan yang rendah diperolehi dengan menggunakan larutan pekat primary polymer PES dan kadar pemilihan O_2/N_2 ialah 1.12 dimana kadar pemisahan untuk O_2 ialah 91.84 GPU dan N_2 ialah 82.07 GPU. Kadar pemilihan mununjukkan tidak banyak perbezaan pada jumlah polymer 25%. Hanya jumlah yang kecil untuk polymer yang kedua ditambahkan kepada polymer yang pertama untuk menghasilkan campuran polymer. Hasil membran kemudiannya akan dianalisa untuk mengenal pasti struktur permukaan dan keratan rentas membran tersebut dengan menggunakan Scanning Electron Microscopy (SEM). Keratan rentas menunjukkan liang bagi campuran polymer adalah kecil berbanding primary polymer manakala struktur permukaan membran yang bersalut adalah lebih licin berbanding yang tidak bersalut. Daripada kajian ini, didapati campuran dua jenis polymer menunjukkan peningkatan terhadap prestasi membran.

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Q	-Flowrate of supplied gas
A	-Area
P	-Trans membrane pressure
α	-Selectivity
	-Permeability of O_2
	-Permeability of N_2

LIST OF ABBREVIATIONS

PES	Polyethersulfone
PSF	Polysulfone
PVDF	Polyvinylidene diflofide
PP	Polypropylene
PI	Polyimide
NMP	N-Methyl-2-Pyrrolidone
PDMS	Polydimethylsiloxane
GPU	Gas Permeation Unit
O_2	Oxygen
N_2	Nitrogen
SEM	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, membrane technology for gas separation and purification process has been interesting. This is mainly due to relatively higher reliability, energy efficiency and lower capital cost than other conventional gas separation process (Paul *et al* and Stern, 1994).

Enriched nitrogen production from air, hydrogen separation in ammonia plants and refineries, removal of carbon dioxide from natural gas, removal of volatile organic compound such as ethylene or propylene from mixture with light gases such as nitrogen in polyolefin purge gas purification and water vapor removal from air are the most widely practice separations (Baker, 2000; Ghosal *et al*, 1994; Zolandz *et al*, 1992).

Membranes have a small footprint where space is limit or where portability. These make them ideal for use in application on offshore platforms, aboard aircraft and refrigerated shipping containers (Baker, 2000).

Many commercial polymeric membrane materials that have good chemical, thermal and mechanical stability is such as polysulfone (PSF), polyethersulfone (PES), polyvinylidene diflofide (PVDF), polypropylene (PP) and nylon

Polymeric materials such as polysulfone (PSF), polyethersulfone (PES) and polyimide (PI) gives high selectivity coefficient and acceptable permeability value for separation of gas mixture (Vu, 2001).

The permeability coefficient will vary from one gas to the next depends on a given polymer and its property that allows the polymer to separate gas mixture.

Oxygen (O_2) is always more permeable than nitrogen (N_2) in all polymers. Ratio of O_2 to N_2 permeability, the selectivity varies from 1.6 to 7.8 with given materials. As the permeability of polymer to oxygen increase, its selectivity will be decrease (Freemen, 1999; Robeson, 1991).

One of the methods to improve the properties of a polymer is by blending with another polymer those posses some desired physical and chemical properties. By using this blending polymer method give ideal separation factor for O_2/N_2 (Ismail *et al*, 2008). Polymer blending method establish as excellent candidate membrane for separation of gaseous mixture in industrial level. Thus, this method can develop in perspective for future commercial application (Kapantaidakis *et al*, 2002).

1.2 Problem Statement

Gas separation with polymer membrane is rapidly becoming a mainstream technology. The main problem in membrane technology is hard to find high performances with both selectivity and permeability. Most of membranes selectivity is inversely proportional with permeability.

PSF and PES are high performance engineering polymer. It has good stability, permeability, selectivity, high critical pressure of plasticization and low cost (Ding *et al* and Ismail *et al*, 2008; Li *et al*, 2004; Kapantaidakis *et al*, 2002).

Polymers with higher gas permeability have lower selectivity (Kapantaidakis, 1999; Robeson, 1991). This fact becomes a factor for looking towards polymer blending methods to combine the properties of different materials and as versatile tool to combine the beneficial properties of two or more components in one single material (Li *et al*, 2001; Park *et al*, 2000).

Therefore, to overcome the problem, by blending the polymer is one of the attractive of tuning the performance of a membrane to achieve the desire for selectivity and permeability of polymer membrane.

1.3 Objective of the Study

Based on problem statement, the objectives of this study are listed as following:

1. To develop asymmetric membrane for O_2/N_2 separation.
2. To compare the membrane performance of difference polymer loading in casting solution.

1.4 Scope of the Study

Several scopes that have been outlined in order to achieve the objective of this study are as following:

1. Make a performance comparison between primary polymers with blended polymer using permeability test.
2. Test the performance of uncoated and coated membrane using O_2 and N_2 gases as a test gas.
3. Characterize the membrane morphology using Scanning Electron Microscopy (SEM).

CHAPTER 2

LITERATURE REVIEW

2.1 Definition of Membrane

Membrane is as a barrier between two fluids where one of the fluids passes the membrane faster than others. Hence, separation occurs. The two fluids will separated into a retentate and a permeate. Retentate is part of the fluid does not pass through the membrane whereas permeate is the part of the fluid that passes through the membrane as show in Figure 2.1 (Mulder, 1996; Baker, 2000 and Naylor, 2004).

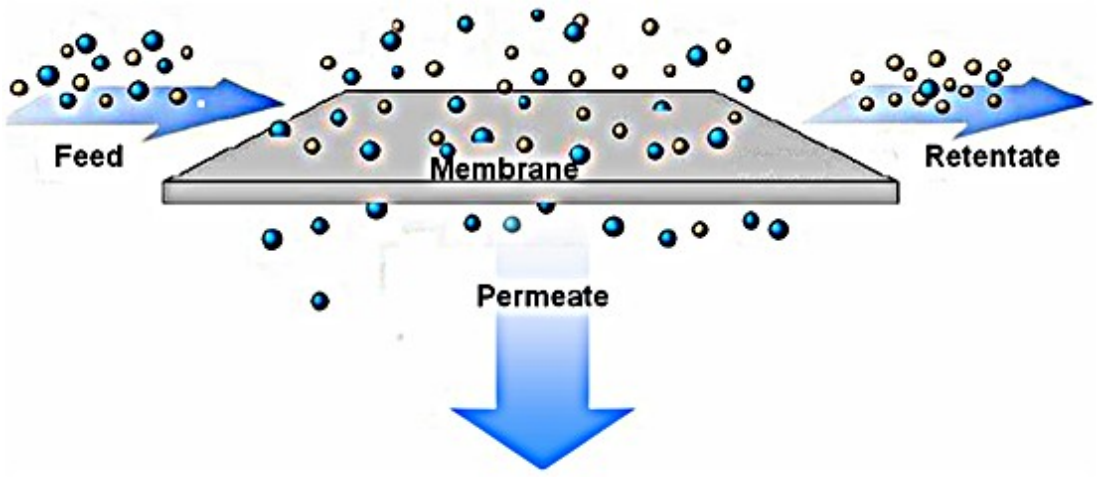

Figure 2.1: Schematic diagram permeation of membrane

2.2 History of Gas Separation

Study of gas separation has a long history but it has become major industrial application of membrane technology only during the past 20 years (Baker, 2000). On 1866, Thomas Graham gave first description of the solution-diffusion model by which the penetrant first dissolve in the membrane and then diffused through by the same process as that occurring in liquids. He demonstrated that atmospheric air could be enriched from 21 % and 41 % oxygen using a natural rubber membrane. He also showed that the permeation rate will effect by the thickness where permeation rate of the gas decrease as the film thickness increase. His work on porous membrane led to Graham's law of diffusion (Baker, 2000 and Naylor, 2004).

Gas separation by polymer was observed by Mitchell in 1891 who found India rubber films permeated CO_2 faster than hydrogen (Naylor, 2004). End of nineteenth and early twentieth century's, the ability of gas to permeate membrane has no industrial or commercial use but the concept is used as theoretical tool to develop physical and chemical theories such as Maxwell's kinetic theory of gas (Baker, 2000).

From 1943 to 1945, for the first time Graham's law of diffusion is used for separation of uranium gas isotopes for uranium enrichment. $U^{235}F_6$ is separate from $U^{238}F_6$. This project is part of Manhattan project (Baker, 2000 and Naylor, 2004). The separation plant, the first large scale membrane that use for gas separation built in Knoxville, Tennessee and for the next 40 years become world largest membrane separation plant (Baker,2000).

In 1940 to 1950, the foundation of modern theories of gas permeation is laid by Barrer, van Amerongen, Stren, Meares and others academic studies (Baker, 2000 and Naylor, 2004). The previous law, Graham's law of diffusion is still accepted for gas transport through membrane. Despite the availability of interesting polymer, to make useful separation membrane systems from these polymers, membrane fabrication technology is not sufficiently advance at that time (Baker, 2000).

Late 1960, techniques developed to produce high flux anisotropic, large surface area, thin and defect free polymeric membrane for reverse osmosis and provided the basis for modern membrane gas separation technology early 1970 (Baker, 2000 and Naylor, 2004). Cellulose acetate for gas dehydration and gas separation are the first polymer to be commercialized. The problem to commercial the gas separation membrane is to economically package large area of membrane. Bray and Westmoreland provided a solution in 1968 the development for reverse osmosis of the spiral wound module. Led to the large scale introduction of gas separation process is due to the development of hollow fibres by Dow and DuPont in between 1968 to 1971. General Electric developed polycarbonate/silicon rubber copolymer was developed for oxygen enrichment of air (Naylor, 2004).

In 1980, Masanto has led to the recent world wide surge in interest in gas separation systems by success in commercializing its Prism membrane which polysulphone with a sealing layer of polydimethylsiloxane for hydrogen sepration (Baker, 2000 and Naylor, 2004). Membrane plant to remove carbon dioxide from methane was built in mid 1980 by Cynara, Separex and Gas Membrane Systems. Although need to face low natural gas price in the 1990, this application grown over the years. At the same time, Dow launched Generon, the first commercial membrane system for nitrogen separation from air. Dow, Ube and DuPont develop materials with improved selectivities since made membrane produce nitrogen was cost competitive (Baker, 2000).

2.3 Membrane Modules

2.3.1 Plate-and-Frame Modules

Plate-and frame modules are one of the earliest modules of membrane system. Membrane, feed spacers and product are layered together between two end

plates. The feed mixture is forced across the surface of the membrane. A portion passes through membrane, enters the permeate channel, and makes its way to a central permeate collection manifold (Baker, 2000 and Naylor, 2004). Figure 2.2 show schematic drawing of plate and frame module.

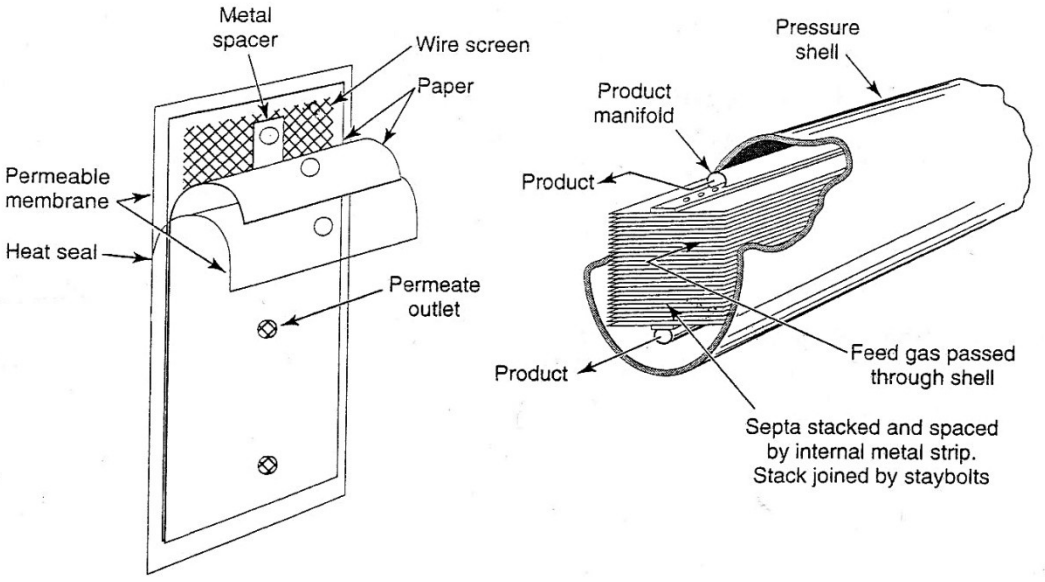

Figure 2.2: Schematic drawing of plate and frame module

2.3.2 Spiral Wound Modules

The spiral wound modules is the next logical step from flat membrane. It is in fact a plate-and frame system wrapped around a central collection pipe, in a similar fashion to a sandwich roll. Membrane and permeate side spacer material are then glued along three edges to built a membrane envelope. The feed side spacer separating the top layer of the two flat membranes also acts as a turbulence promoter (Baker, 2000 and Naylor, 2004). This module is shown schematically in Figure 2.3.

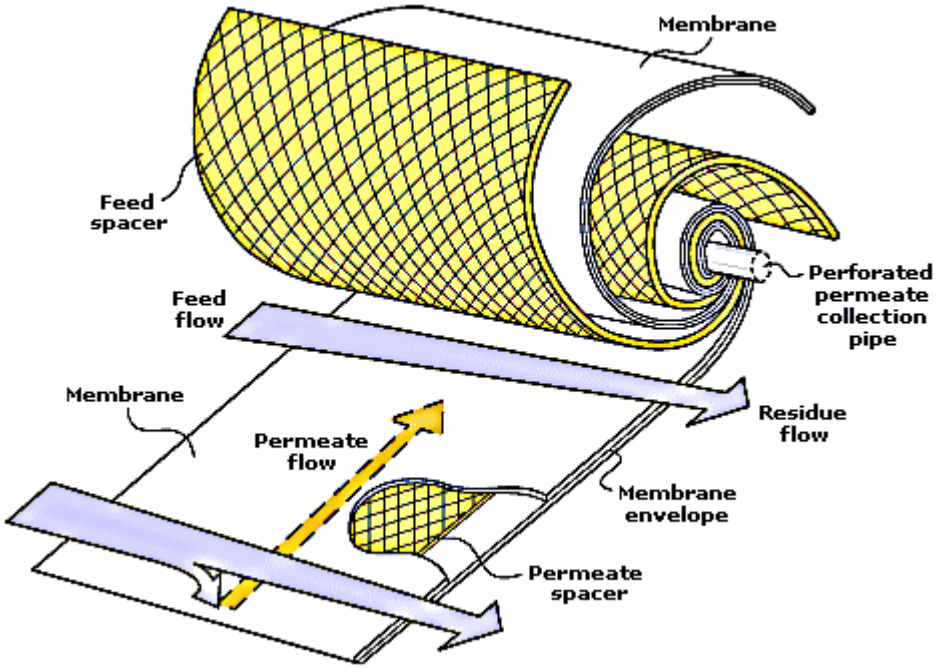

Figure 2.3: Schematic drawing of spiral wound module

2.3.3 Hollow Fiber Modules

Hollow fiber membrane modules are formed in two basic geometries. The first is the shell side feed design illustrated in Figure 2.4. A loop or a closed bundle of fibers in contained in a pressure vessel. The system is pressurized from the shell side. Permeate passes through the fiber wall and exits through the open fiber ends. This design is easy to make and allows very large membrane areas to be contained in an economical system. Because the fiber wall must support considerable hydrostatic pressure, the fibers usually have small diameters and thick walls, typically 50 m internal diameter and 100 to 200 m outer diameter (Baker, 2000 and Naylor, 2004).

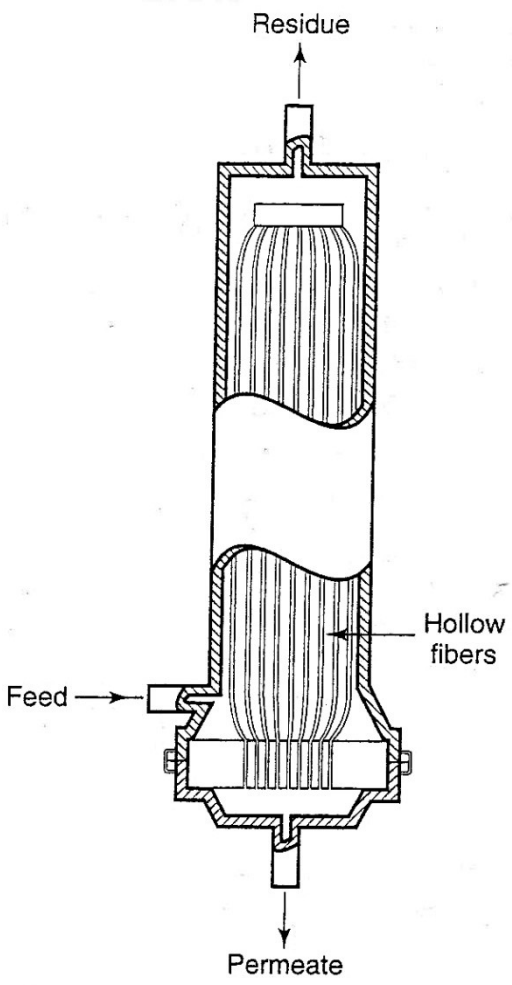

Figure 2.4: Illustrated design of hollow fiber module, shell side feed

The second type of hollow fiber module is the bore side feed type illustrated in Figure 2.5. The fibers in this type of unit are open at both ends, and the feed fluid is circulated through the bore of the fibers. To minimize pressure drop inside the fibers, the diameter are usually larger than those of the fine fibers used in the shell side feed system and are generally made by solution spinning. These called capillary fibers that used in ultrafiltration, pervaporation and some low to medium pressure gas application. Feed pressures are usually limited to below 150 psig (Baker, 2000 and Naylor, 2004).

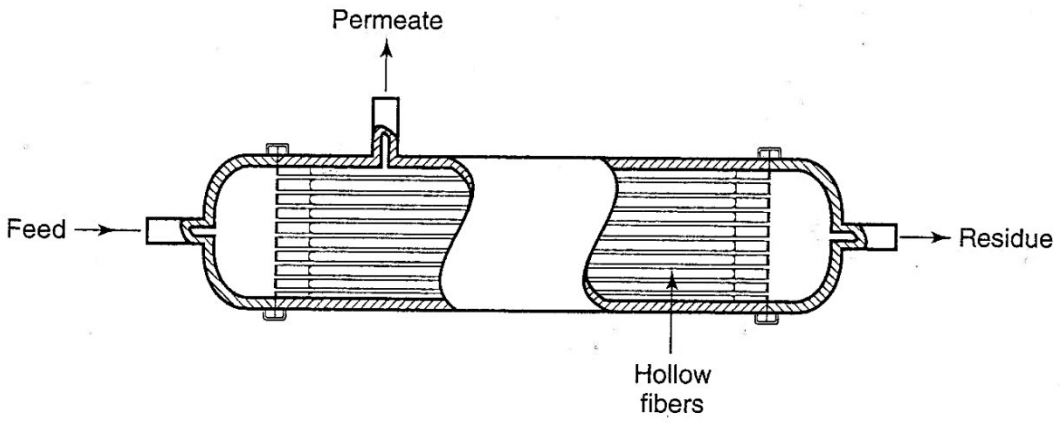

Figure 2.5: Illustrated design of hollow fiber module bore side feed

2.3.4 Tubular Modules

Tubular modules are now generally limited to ultrafiltration application, for which the benefit of resistance to membrane fouling due to good fluid hydrodynamics outweighs their high cost (Baker, 2000). Typically, membranes are placed inside a porous stainless steel, ceramic or plastic tube with the diameter of the tube that generally more than 10 mm. the number of tube put together in the module may vary from 4 to 18, but is not limited to this number as shown in Figure 2.6 (Baker, 2000 and Naylor, 2004).

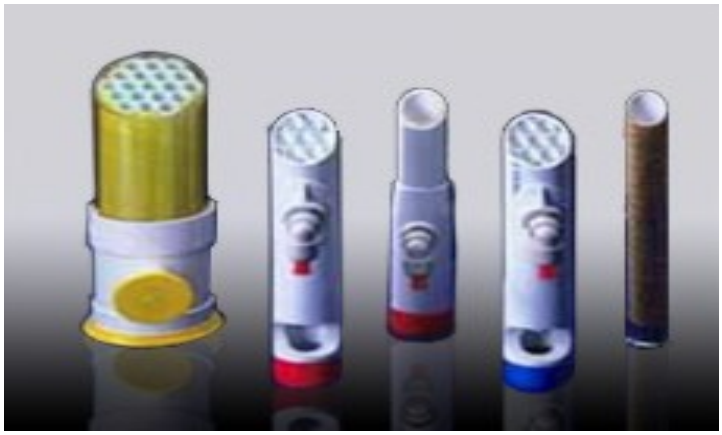

Figure 2.6: Typical tubular module design

2.4 Membrane Materials

2.4.1 Polymeric Membrane

Most gas separation processes require that the selective membrane layer be extremely thin to achieve economical flux. Typical membrane thicknesses are less than 0.5 m and often less than 0.1 m. Early gas separation membranes were adapted from the cellulose acetate membrane for reverse osmosis (Baker, 2000).

Gas separation membranes are sensitive to minor defect shown in Figure 2.7, such as pinholes in the selective membrane layer, than membranes used in reverse osmosis or ultrafiltration. Small defect can highly decrease the selectivity of gas separation membranes. For early developer, the sensitivity of gas separation membranes to defects becomes a serious problem. Moreover, few defects are very difficult to avoid during membrane preparation and module formation. So that, coating is the solution to plugged membrane defect by apply thin layer of coating agent such as silicon rubber to the membranes (Baker, 2000).

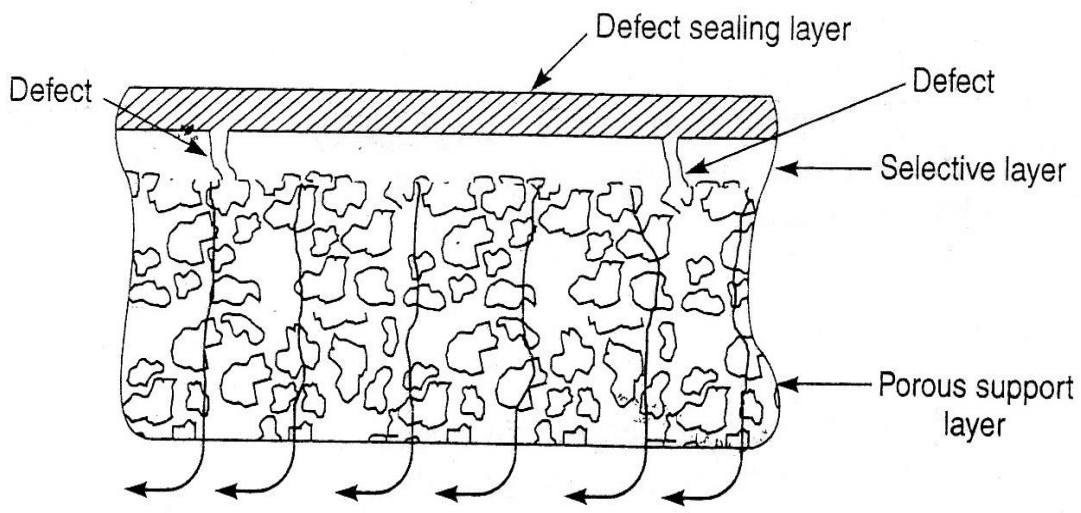

Figure 2.7: Schematic drawing of defect sealing on selective layer